A Complete Thermal Processing System for Fuels and Polymer Analysis

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Thermal Characterization of fuel sources is essential in geochemical exploration. Determining the maturity of source rock and coal beds aids in the processing of these fuel sources. Quantitative assessment of the migratory hydrocarbons (P_1), kerogen (P_2) and fixed gases (P_3) provide vital information about the fuel generating capability of the sample.

Total thermal processing of samples, both geochemical and polymeric, can occur with temperatures up to 1400°C. The system used in this evaluation makes use of both furnace and filament pyrolysis. Samples analyzed included oil shales, polymers and composite materials.

Pyrolysis equipment in general is composed of three major components. First and foremost, a filament, wire or furnace in which the sample is deposited for pyrolysis. The second component is a heated chamber which prevents the pyrolysate from condensing and not reaching the injection port. The final component is a modification or add-on to the injection port of the gas chromatograph [1-3]. Egsgaard and Carlsen describe a low pressure continuous flow inletting system for Curie Point pyrolysis into a mass spectrometer [4]. In their work they describe three separate inletting systems depending on sample matrix: gas, liquid or solid. Many mass spectrometers, however, can accommodate direct insertion probes for pyrolysis in the source [5,6]. This technique, although valuable for many applications, tends to produce highly complex spectra because there is no chromatographic separation. Cold trapping prior to injecting the pyrolysate onto the GC will improve resolution, however, highly volatile components may tend to breakthrough and go undetected.

The impetus of his work was to provide an analytical system which would provide a full range of thermal processing capabilities, including dynamic headspace, furnace pyrolysis and filament pyrolysis. Previously, thermal treatment of samples involved Curie Point, furnace or filament pyrolysis. Each of these pyrolysis techniques has advantages and limitations.

The system in this study makes use of a programmable furnace pyrolyzer for temperatures up to 600°C and a filament pyrolyzer capable of reaching temperatures up to 1400°C. A major benefit of this system is the programmable furnace in combination with a series of adsorbent traps which enable fractions to be collected prior to chromatographic analysis.

All heated zones in the system are controlled via the systems computer terminal which can accommodate 20 separate methods. As the sample is heated, sample flow passes over the sample and sweeps the volatiles through an adjustable split valve. Part of the sample then moves to a monitor flame ionization detector (FID), the rest of the sample is carried to an absorbent trap. At that point a second temperature fraction can be collected in the same manner. A molecular sieve trap can also collect any fixed gases which may be evolved from the sample. These gases are then analyzed by a self contained packed column GC with a thermal conductivity detector. This is the first analytical system to employ furnace pyrolysis, filament pyrolysis and trapping capabilities. Heating rate capabilities range form 0.01°C/ minute to a maximum rate to 20,000°C/second.

Experimental Section

The system described in this paper makes use of existing elements of analytical instrumentation in a unique combination. A CDS Instruments Model 920 Thermal Processing System was used in these experiments. Dynamic headspace/purge and trap, furnace pyrolysis and filament pyrolysis can all be performed during a single experiment.

The thermal processing unit consists of a thermal desorption/furnace pyrolysis chamber mounted on the side of the instrument. For dynamic headspace and/or furnace pyrolysis the chamber has a maximum temperature of 600°C. The heating rate of the furnace is up to 60°C/minute. If higher temperatures or heating rates are required, the Pyroprobe 2000 can be used to heat the sample to a maximum temperature to 1400°C at rates from 0.01°C/minute to 20,000°C/second. As the sample is heated, carrier flow directs the volatiles to the three on-line traps. These traps contain Tenax TA to retain organic fractions or molecular sieve 5A for trapping fixed gases.

Figure 1 shows a flow diagram for this system, which contains three traps, a monitor FID, packed column GC with a TCD and a capillary column GC with an FID. In terms of geochemical analysis, the furnace heats the sample to 300°C, while the migratory hydrocarbons are trapped onto trap A. At the same time part of this fraction goes on to a monitor FID to determine the total P_1 concentration. The sample is then heated to 600°C. The cracked kerogen passes to a split valve where part of the sample is collected onto trap B and the remainder passes on to the monitor FID for P_2 evaluation. After collection of the fixed gases on the molecular sieve trap, the fixed gases are analyzed with a packed column GC and a thermal conductivity detector. After this, the trap containing the migratory hydrocarbons (P_1) is backflushed through a heated transfer line to a capillary GC with a 50M X 0.25mm SE-54 capillary column. After this analysis, trap B containing the cracked kerogen components is backflushed and analyzed by the capillary GC.

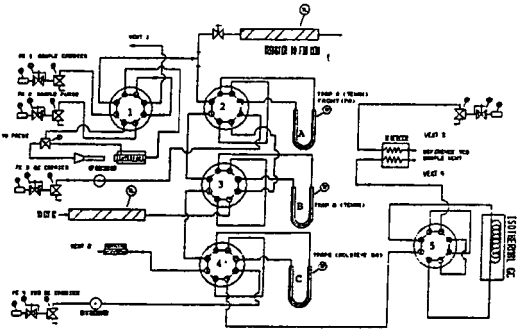

Figure 1: Flow schematic of thermal processing system.

Due to the flexibility and programming capability of this system, any number of thermal treatments can be performed depending on analytical needs.

Results

Two geochemical samples were compared in this study. The first sample was an Alaskan oil shale, the second sample was from the Green River. The samples were heated to 300°C and then to 600°C using the furnace pyrolyzer. Figure 2 shows the monitor FID composite results of the Alaskan oil shale sample along with the temperature profile. The P_1 composite fraction elutes at approximately 138°C and P_2 elutes at a sample temperature of 530°C. The area ratio of P_1/P_2 was measured to be 0.084.

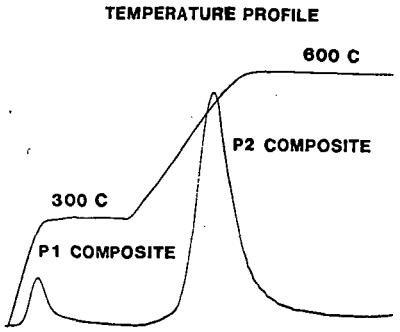

Figure 2: Temperature profile, P_1 and P_2 fractions of an Alaskan oil shale.

Figures 3 and 4 respectively, show the capillary column chromatograms of these two fractions. The P_1 fraction shows the migratory hydrocarbons from pentane to tetradecane. The larger fraction, P_2 displays the cracked kerogen geopolymer. Compounds generated by thermal treatment up to 600°C produces hydrocarbons up to C_{30}.

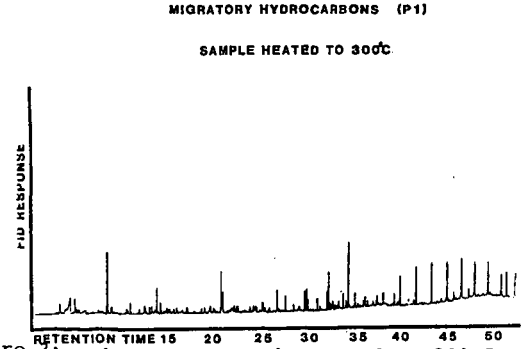

Figure 3: Alaskan oil shale heated to 300 C.

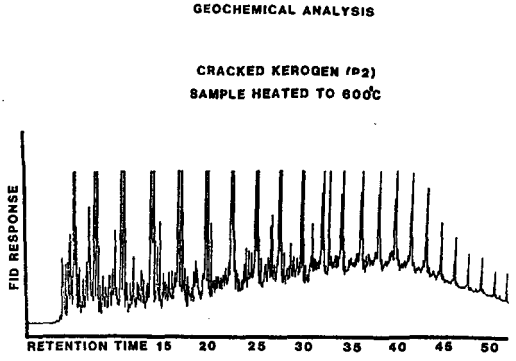

Figure 4: Alaskan oil shale heated to 600 C.

A second application of this instrument is in the field of synthetic polymer analysis. Residual solvent analysis, polymer identification and structural determinations are all possibilities. Figure 5 displays a 10 mg. sample of polystyrene which was heated to 300°C. The chromatogram shows primarily solvents used in the processing of this polymer and especially residual styrene monomer.

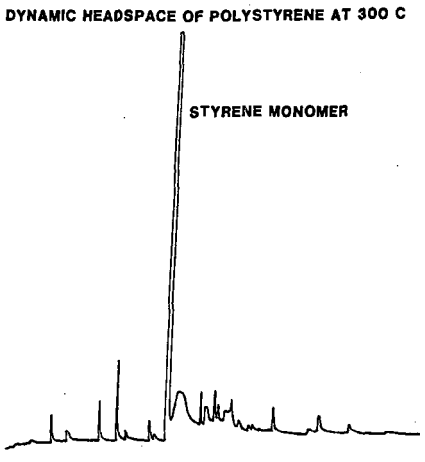

Figure 5: Polystyrene heated to 300 C for 10 minutes.

After residual solvent analysis, a portion of the residue (approximately 500 micrograms) was pyrolyzed at 750°C for 10 seconds. Figure 6 shows the results of this procedure. Styrene monomer, dimer and trimer are all products of this thermal treatment.

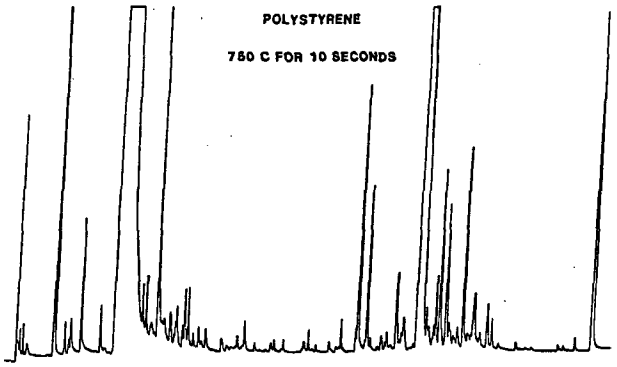

Figure 6: Pyrolysis/GC analysis of polystyrene at 750 C.

Finally, the most complex type of analysis involves composite materials which contain many components of varying volatilities. Cosmetics are a group of materials which fit ideally into this category. Mascara samples frequently contain solvents, pigments, polymers and inorganics which can hinder the analysis. A mascara sample was heated to 300°C and then pyrolyzed at 700°C for 10 seconds. The solvent analysis of the mascara sample is shown in figure 7. This chromatogram reveals solvents and the black pigments used in this commercial product. Subsequent pyrolysis of the residue, figure 8, shows the presence of an acrylate polymer which was identified as polymethylmethacrylate.

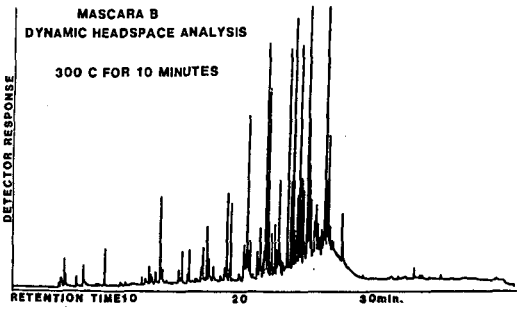

Figure 7: Dynamic headspace of mascara at 300 C.

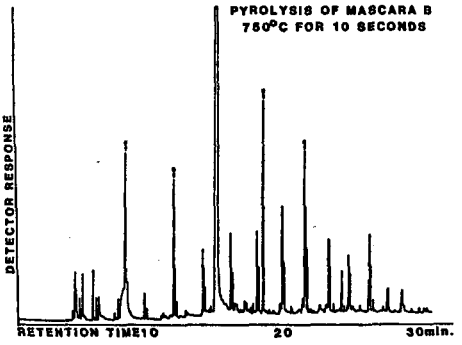

Figure 8: Pyrolysis/GC analysis of mascara residue.

Conclusions

The analytical system described in this paper proves to be versatile instrument for the thermal processing of a diverse range of samples. Due to the trapping capabilities of the system, several temperature dependent fractions can be collected an subsequently analyzed by GC, GC/MS or GC/FT-IR.

References

(1) Hickman, D.S.; Jane, I., Analyst, 1979, 104, 334

(2) Ohtani, H.; Nagaya, T.; Sugimura, Y, Tsuge, S. J. Anal. Appl. Pyrol., 1982, 4, 117.

(3) Washall, J.W.; Wampler, T.P. J. Chromatogr. Sci. 1989, 27, 144.

(4) Egsgaard, H.; Carlsen, L. J. Anal. Appl. Pyrol. 1984, 7, 1.

(5) Westall, W.A.; Ridduck, A.J. J. Anal. Appl. Pyrol. 1987, 11, 3.

(6) Montaudo, G. J. Anal. Appl. Pyrol. 1988, 13, 1.

(7) Whiton, A.S.; Morgan, S.L. Anal. Chem. 1985, 57, 778.